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(54) Optical device with a coating having a continuously varying refractive index

(57) An optical device comprises a substrate having first mechanical and/or chemical characteristics and a coating, such as a wear-resistant coating, having different characteristics. To maintain good light transmission qualities when the refractive indices of the substrate material and of the coating surface are different, the refractive index of the coating is continuously varied from that of the substrate to the desired final value at the coating surface. A method of producing the coating by plasmapolymerisation comprises the step of increasing the proportion of at least one first monomer gas in the process atmosphere while simultaneously reducing the proportion of at least one second monomer gas. Preferred monomer gases include metalorganic compounds of titanium or silicon. Other monomers used are alkanes, alkenes, alkynes, alcohols, amines, ketones and aromatic compounds, eg toluene.

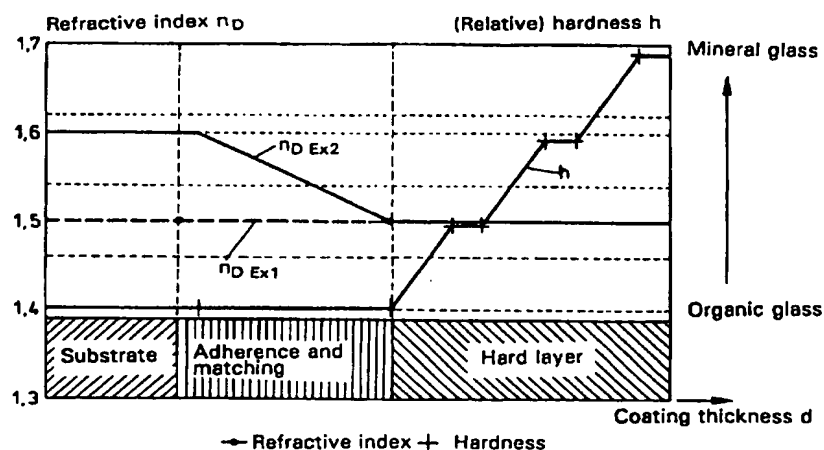


FIG. 4

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1/4

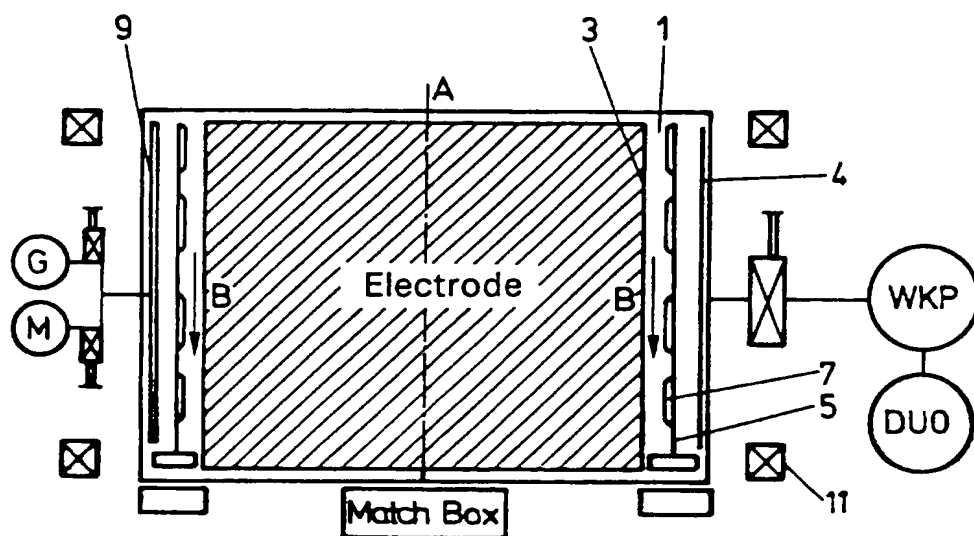
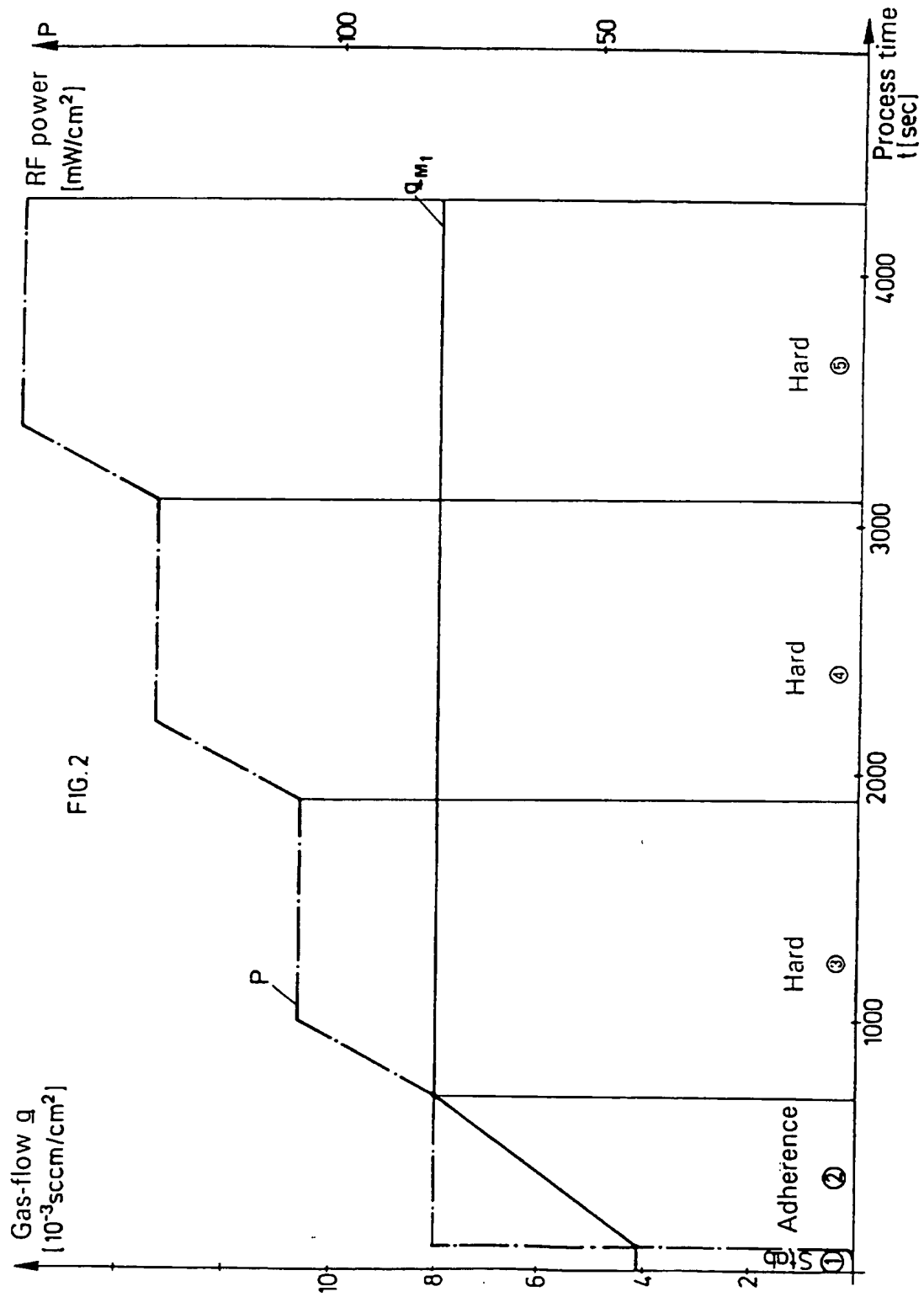
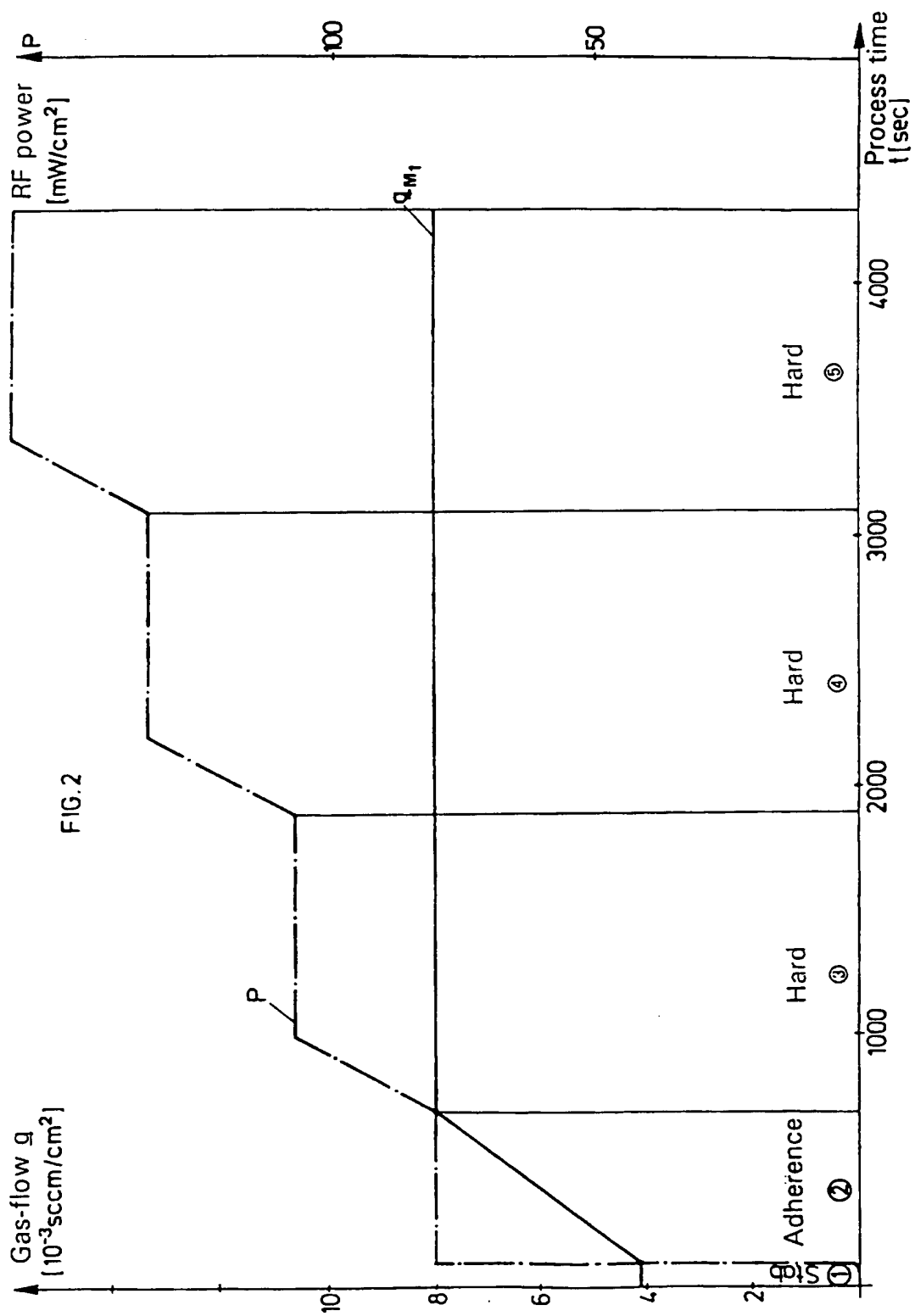


FIG.1

2/4





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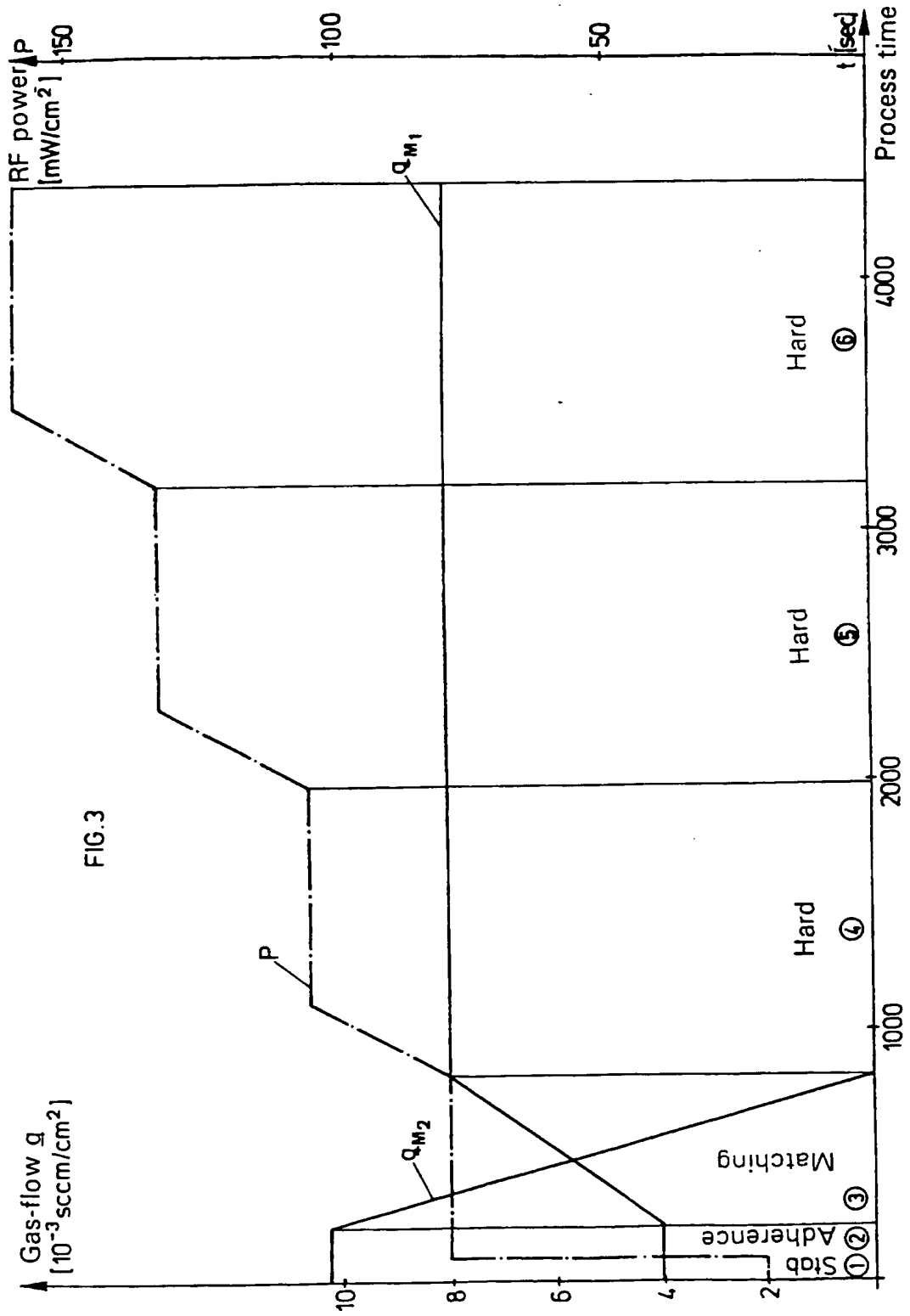


FIG.3

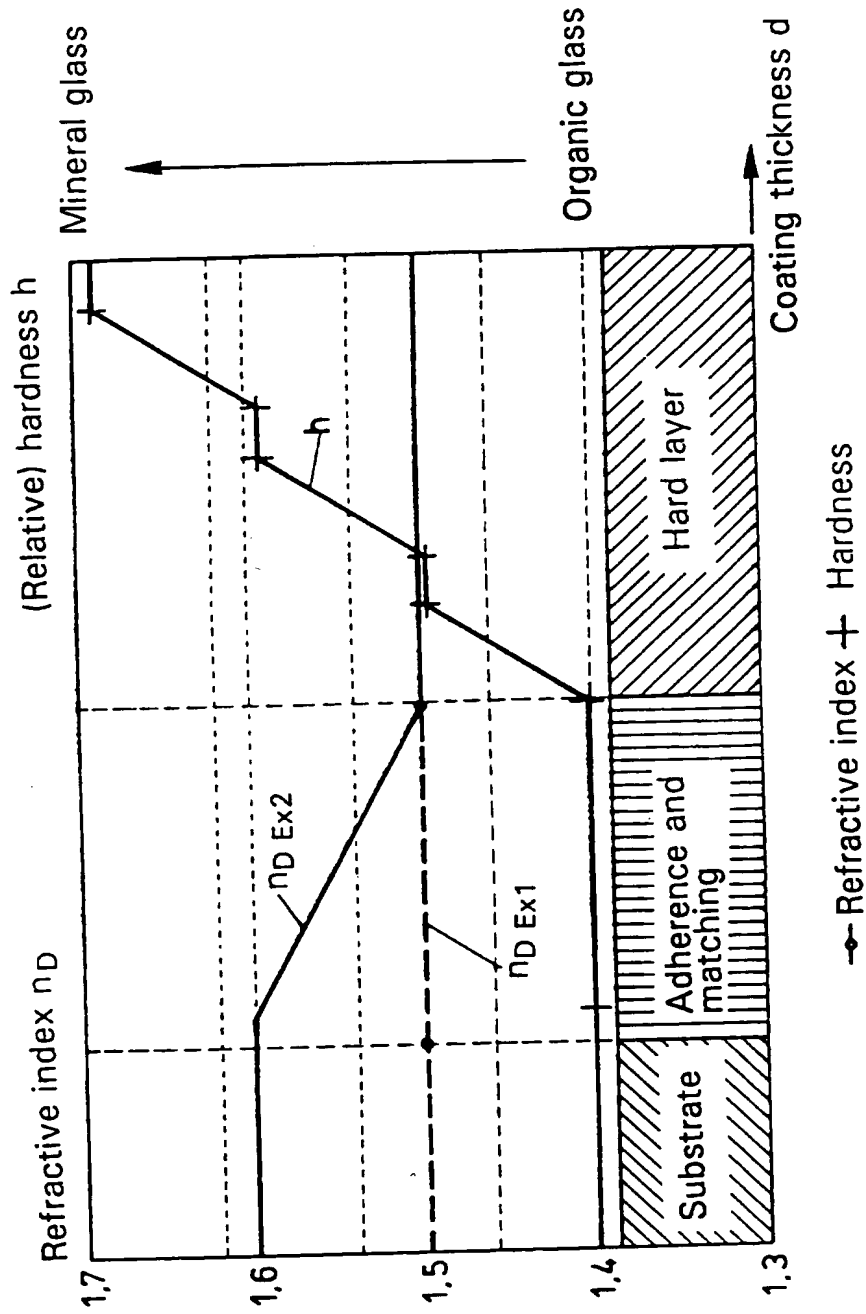


FIG.4

TITLE:

Optical device and method for coating an optical substrate

BACKGROUND OF THE INVENTION**Field of the Invention**

The present invention is generally directed to thin-film coating of carrier substrates for optical devices. More specifically, it is directed to an optical device which comprises a carrier substrate with a surface consisting of a material with a predetermined index of refraction and with a first set of mechanical and/or chemical characteristics, whereby the surface of the carrier substrate is coated, the surface of the coating remote from the surface of the substrate having a second set of mechanical and/or chemical characteristics different from the first set of characteristics.

It is further directed to a method for coating optical substrates by plasmopolymerisation.

Definitions

- Throughout the present description, the expression "process atmosphere" means the composition of the atmosphere wherein plasmopolymerisation occurs.
- Throughout the present description the expression "process parameter" means a physical quantity that controls the plasmopolymerisation process, as e.g. total pressure in the plasmopolymerisation process area, strength of magnetic field prevailing in said area, RF power applied between plasma generating electrodes in said area.

DESCRIPTION OF THE PRIOR ART

Coated devices in which mechanical and/or chemical characteristics of a substrate surface are altered by providing a coating are commonly known. Under mechanical or chemical characteristics, characteristic behaviour is understood as mechanical wear resistance, chemical wear or corrosion characteristics, adherence characteristics, diffusion characteristics, wettability characteristics etc.

Optical devices are known in which a coating changes the mechanical and/or chemical characteristics of the substrate surface whereon the coating is applied, be it that the coating is directly deposited on the surface of the substrate or be it that the coating is applied on a further coating, which is directly applied to the surface of the substrate. The body on the surface of which the coating is applied is generally termed the "substrate" throughout the following description.

For mechanical wear protection, hard material coating of optical plastic bodies with lacquer is customary for the production of planar plastic substrates and in ophthalmics. Lacquers with different indices of refraction are used therein.

The method for producing mechanical and chemical wear resistant coatings on different substrates by means of plasmopolymerisation has also been known for quite a long time. Under the term "plasmopolymerisation" one understands generally coating formation from vapour of organic or metal-organic monomers in a plasma discharge. With respect to such coating methods, attention is drawn to R.D. Agostino, "PLASMA DEPOSITION TREATMENT AND ETCHING OF POLYMERS", Academic Press, 1989, ISBN 0-12-200430-2; and to H. v. Böhning, "PLASMA SCIENCE AND

TECHNOLOGY", Cornell University Press, 1982, ISBN 0-8014-1356-7.

From EP-A-0 177 517 and from the IKV Final Report "Plasmapolymerisation" from K. Telgenbüscher, J. Leiber, May 19, 1993, Institute for Plastic Material Treatment, Aachen methods are known in which by varying specific coating process parameters such as power or the process atmosphere, as by deferred admission of oxygen, a good adhesion of the coating is obtained and thereby simultaneously a high wear resistance. Therein, exclusively silicon-containing organic compounds are used as metal-containing monomers. By means of the said variations, it is attempted to obtain a change in the mechanical characteristics.

For instance, the growth of the coating is controlled so that it starts with a relatively soft adhesion improving coating on a substrate which is relatively soft, which is realized in a process atmosphere that contains a silicon-containing metal organic compound without admission of oxygen. Afterwards, step by step or continuously, oxygen-flow is increased, whereby the quotient Si/O decreases in the coating, which leads to an increase of coating hardness and thereby of mechanical wear resistance.

If the finishing coating is applied with a high enough oxygen content in the process atmosphere and thickly enough, satisfactory mechanical wear protection of a plastic material substrate can be obtained.

With respect to the deposition of TiO_2 or of a TiO_2 -containing coating by means of plasmapolymerisation, attention is drawn to different basic investigations, for instance in H.J. Frenck, W. Kulisch et al., Thin Solid

Films, 201 (1991) 327-335; J.P. Barker, P.J. Radcliff et al., Proceedings of 11th International Symposium of Plasma Chemistry, August 22-27 (1993) 1154-1159, ISBN 0-95221-493-8.

Principally, it is further known to use plastic substrates for ophthalmic applications such as lenses and to provide such substrates with a wear protective layer.

One plastic material which is often used for ophthalmic applications is the relatively low-weight plastic material CR-39 which has good optical characteristics. The index of refraction of this plastic material is 1.5.

Customarily, such plastic material bodies are wear resistant coated by means of a coating containing a silicon organic material with an index of refraction of approximately 1.5.

Thus, such a substrate coated with such a coating inherently leads to an optical device with no discontinuity in refractive index and thus with no disturbing interference pattern and no reduction of transmission. It thus may not address the problem of discontinuous index of refraction that must be resolved when such a discontinuous index could in fact occur.

The use of substrates with higher index of refraction would be most desirable because of the resulting reduced substrate thickness. Use of such higher index substrates is nevertheless known but thereby the occurrence of interference disturbances is tolerated in view of the reduced thickness achieved.

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SUMMARY OF THE INVENTION

It is a predominant disadvantage of the described coated optical devices that by applying the coating, for instance a wear resistant coating, a stepped characteristic of the index of refraction occurs considered along the carrier substrate and the coating applied thereto. Thus, optical characteristics of a resulting optical device, too, are changed by a coating which has principally been applied with the aim of changing other characteristics than optical ones, namely to change mechanical and/or chemical characteristics of the substrate.

It is thus a general object of the present invention to provide an optical device and a method of producing such device, whereby the coating changes exclusively that characteristic wherefore it is applied, thus for instance exclusively the mechanical or chemical wear resistance characteristic, adherence characteristic, corrosion characteristic, diffusion characteristic or characteristics of wettability.

This is achieved by the optical device according to the present invention, which comprises a carrier substrate with a surface consisting of a material with a predetermined index of refraction and with first mechanical and/or chemical characteristics, whereby the surface of the carrier substrate is coated and the surface of the coating remote from the surface of the substrate has second mechanical and/or chemical characteristics which are different from the mentioned first characteristics and wherein further the index of

refraction departing from the predetermined index of refraction of the carrier substrate surface material varies continuously through at least a part of the coating up to the final index of refraction at the external surface of the coating. The object of providing a method of production of optical devices, that fulfil the above mentioned object, is achieved by a method for coating an optical substrate by plasmapolymerisation, which comprises the steps of controlling the index of refraction along the growing coating so as to vary continuously from the index of refraction of the substrate to an intended final index of refraction of the coating at its surface by controlling the composition of the atmosphere of plasmapolymerisation and/or by controlling at least one process parameter for the plasmapolymerisation coating process.

All the objects, advantages and preferred features of the inventive optical device and method for producing such will become evident to the person skilled in the art when reading the description and claims of the present application.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention, under all its aspects, will be better understood and objects other than those set forth above will become apparent to the person skilled in the art when consideration is given to the following detailed description thereof. Such description makes reference to the annexed drawings wherein:

Fig. 1 schematically shows a plasmapolymerisation apparatus which accords with that described in EP-A-0 550 003 (or US-A-5 310 607) and which is operated according to the DE-A-39 31 713 (or US-A-5 227 202);

Fig. 2 shows the control of process atmosphere with respect to time for a prior art resistance coating of plastic material lenses with an index of refraction $n_D = 1.5$;

Fig. 3 shows, in a representation analogous to that of Fig. 2, a process according to the present invention for plastic material substrates with $n_D > 1.5$;

Fig. 4 shows along the thickness dimension of the coating of an optical device according to Examples 2 and 3 of the invention the profile of the index of refraction n_D and of the relative hardness h .

Fig. 1 schematically shows a prior art plasmapolymerisation apparatus which is preferably used for the inventive method to produce the inventive optical device. This apparatus accords with the apparatus of the types PPV 100, PPV 500 or PPV 1000 of Balzers AG.

The process area 1 has an annular configuration. Its interior wall is, at least in part, formed by the first electrode arrangement 3 and its outer wall by the second electrode arrangement 4. Within the process area 1 an RF plasma discharge is generated, electrically fed by an RF signal of preferably 13.56 MHz. The discharge is thereby homogeneously distributed along the entire annular process area 1. In the middle of the process area 1, there is provided an annular substrate carrier 5 on which substrates 7 are held along their edges. The substrate carrier 5 slowly rotates within the annular process area 1. Thereby and as is described in EP-A-0 550 003 (corresponding to US-A-5 310 607) and DE-A-39 31 713 (corresponding to US-A-5 227 202) there is achieved all around the substrate a simultaneous and at least nearly equal plasmapolymerisation coating with the exception of surface areas of the substrates along which the substrates are held by the substrate carrier 5.

The process atmosphere in the process area 1 is given by

feeding gases or gas mixtures through a gas feed arrangement 9 into the process area. Coils 11 generate in the process area 1 a magnetic field B with lines of field substantially parallel to the central axis A of the annular apparatus configuration.

At G, there is schematically shown a gas tank with a controllable outlet; and M shows a monomer tank. The process atmosphere is open-loop controlled or negative feedback controlled to a desired composition. Preferably and in a well-known manner, the process atmosphere is monitored and negative feedback controlled.

In the following Table I, the characteristic data of the apparatus used in the following examples and according to Fig. 1 are shown.

Table I

Type of apparatus	Volume [l]	Capacity for Lenses with \varnothing 60	RF-Power [W]	Magnetic Field [mT]	Pumping Power [m ³ /h]	No. of Gas feeds
PPV 100	20	12	1250	0-17	400	3
PPV 500	70	96	2500	0-7	2000	3
PPV 1000	215	192	5000	0-17	4000	3

In Table II, seven settings or process atmospheres are shown, together with process parameters and the resulting index of refraction of the coating resulting from plasmapolymerisation obtained in an apparatus PPV 100. These different settings and the resulting indices of refraction show principally that by varying the process atmosphere and/or process parameters, accurate and small variations of the index of refraction in the deposited coating may be achieved.

Table II

No.	n_D	Pressure	Magnetic field	RF-Power	RG-Flow	M1-Flow	M2-Flow	M3-Flow
		[10 ⁻² mbar]	[mT]	[mW/cm ²] *	[sccm/cm ² x 10 ⁻³] *	[sccm/cm ² x 10 ⁻³] *	[sccm/cm ² x 10 ⁻³] *	[sccm/cm ² x 10 ⁻³] *
1	1.50	1.2	4.0-5.0	80	-	4.3	-	-
2	1.56	1.9	3.5-4.5	80	-	3.7	5.4	-
3	1.60	1.5	3.5-4.5	80	-	3.2	10.6	-
4	1.65	1.4	ca. 2.0	95	-	1.3	-	1.9
5	1.67	1.4	ca. 1.4	95	-	1.3	-	1.9
6	1.72	1.3	ca. 2.0	160	-	-	-	1.9
7	1.80	1.4	ca. 1.4	130	5.8	-	-	1.9

*Power and flow relate to the respective electrode surface.

Therein:

- M₁ stands for dimethyldiethoxysilane,
- M₂ stands for toluene,
- M₃ stands for titanium(IV)-isopropylate and
- RG stands for O₂.

These symbols M₁, M₂, M₃, RG are used throughout the further description in the sense given above. Nevertheless, and as will be also described below, other gases or monomers may be used to perform the inventive method and to produce the inventive optical devices.

Preferably monomers are used which have a sufficient stability and relatively high vapour pressure and further have low toxicity, which are common and which are thus relatively inexpensive. Thus, principally and for performing the inventive method, the following monomers may be used:

- purely organic base substances: alkanes, alkenes,

alkynes, alcohols, amines, ketones, cyclical or anti-cyclical compounds and aromatic circular compounds, aliphatic, alicyclic or aromatic compounds;

- Metalorganic compounds, especially silicon and titanium containing compounds with the following structures:
- $\text{TiR}_x(\text{OR})_y$ with $0 \leq x, y \leq 4, x + y = 4$,
as e.g. $\text{TiR}_4, \text{Ti}(\text{OR})_4$,
- $\text{R}_{x1}(\text{OR})_{y1}\text{SiOSiR}_{x2}(\text{OR})_{y2}$ with
 $0 \leq x_1, y_1 \leq 3; x_1 + y_1 = 3;$
 $0 \leq x_2, y_2 \leq 3; x_2 + y_2 = 3;$
as e.g. $\text{R}_3\text{SiOSiR}_3, (\text{RO})_3\text{SiOSi}(\text{OR})_3$,

whereby R stands for an organic group.

One or more than one organic group R may be replaced by hydrogen atoms and different organic groups R may be linked to a metal atom and/or one or more than one hydrogen atom may be linked to a metal atom.

Controlling the coating process according to the example process control settings as defined under the numbers 1 to 7 of Table II results in the respective indices of refraction n_D as listed in that table, so that one can select respective process control settings and/or interpolate between such settings so as to control a desired profile of index of refraction during deposition of the coating.

As has been described, the inventive method is not limited to the use of the monomers M_1, M_2, M_3 or of the reactive gas RG, as shown in Table II and as defined, but other substances may be used so that each desired value

of index of refraction between 1.4 and 2.2, but especially between 1.45 and 2, may be realized for the coating. If desired, beside the monomers in gaseous state, one or more than one gas, especially oxygen or nitrogen, may be fed to the process atmosphere.

DEFINITION OF TESTS WHICH WERE PERFORMED ON THE COATED PLASTIC MATERIAL BODIES

1. Optical Characteristics

1.1 Transmission

The transmission was tested with test light with an optical wave length $\lambda = 550$ nm.

The following is to be considered:

The minimum reflection of a homogenous body for light impinging at 90° and at ambient air is determined by the change in index of refraction n_D at the body's surface.

If a body is coated and because of a change in index of refraction at the interface between substrate and coating the transmission is reduced, then the resulting reflection is higher than the reflection defined solely by the characteristics of the coating/air interface.

This means for the present invention:

The smaller the steps in refractive index along the test light beam path through coating and substrate, the closer will be the measured transmission to that transmission which is defined

solely by the index of refraction at the external surface of the coating.

1.2 Newton Ring Pattern

If the coated body has a discontinuous profile of index of refraction with a discontinuity especially at the coating/substrate interface, a so-called Newton ring pattern will appear if such a body is examined by eye. Such pattern is caused by interference phenomena.

2. Test of Mechanical Resistance

The rubber-gum test according to DIN 58196-4 or ISO 9211-4, MIL 657 has been performed.

Example 1: (Prior Art)

With an apparatus PPV 1000 a CR-39 plastic material substrate was coated with a wear protective coating. The index of refraction of CR-39 is 1.5. In Table III, the coating parameters and the timing sequence of their controls are listed.

Table III

Coating Module/ Type	Duration	Pressure	Magnetic- Field/Ramp Duration	RF-Power P/Ramp Duration	RG flow/ Ramp Duration	M1 Flow/ Ramp Duration
1 Gas stabil.	90	0.8	4.0-5.0	-	-	4.2/0
2 Adherenc.	600	1.2	4.0-5.0	80/0	-	8.0/600
3 Hard	1200	2.0	4.0-5.0	106/300	3.2/300	8.0/0
4 Hard	1200	2.4	4.0-5.0	133/300	6.4/300	8.0/0
5 Hard	1200	2.7	4.0-5.0	160/300	12.2/300	8.0/0

Therein the following dimensions are used, as well as in examples which will be described later:

Time duration:	sec
Pressure:	10^{-2} mbar
Magnetic Field:	mT
RF-Power P:	mW/cm ² -electrode surface
Flow:	10^{-3} sccm/cm ² -electrode surface
Ramp rise duration:	sec

Optical tests of the coated CR-39 substrates showed that these coated substrates have a high transmission of 92%. No Newton ring pattern could be recognized. No damage was caused by the rubber-gum test to the coated substrate, in contrast to significant damage to the uncoated CR-39 substrate by rubber-gum traces.

It is known that the index of refraction of silicon organic wear protective coatings is approximately 1.5, thus equal to that of the CR-39 plastic material.

Thus, the coating air interface would lead to a reflection of 8%, and the measured transmission of 92% clearly shows the constant profile of index of refraction at a value of 1.5 through the substrate and the wear protective coating. This accords with the explanations given above with respect to silicon organic wear protective coated CR-39 plastic material substrates.

Higher refractive index plastic material substrates are commonly used, as described in the following, for instance, with an index of refraction $n_D > 1.6$, because optical lenses of such material will be thinner and lighter. These advantages could only be exploited up to now together with toleration of the disadvantages of reduced transmission and of interference effects, which

are both due to the commonly encountered refractive index step at the substrate/coating interface.

Because such higher refractive index substances are additionally softer than lower index substrates, a wear protective coating for such higher index substrates is a necessity, e.g. for the higher refractive index substrates which will be described, namely of HI-plastic material.

The timing sequence of the coating process according to Table III for the prior art process and optical device is shown in Fig. 2.

Example 2: (Example of Inventive Method and Device)

With a PPV 1000 plasmapolymerisation apparatus, HI-plastic material substrates with a higher index of refraction, namely $n_D = 1.6$, were coated with the wear protective coating according to the coating parameters listed in Table IV.

Table IV

Coating Module	Dura- tion	Pres- sure	Magnetic Field/ Ramp-	RF- Power P/Ramp-	RG- Flow/ Ramp-	M ₁ - Flow/ Ramp-	M ₂ - Flow/ Ramp-
No. Type			Duration	Duration	Duration	Duration	Dura- tion
1 stab.	90	0.8	4.0-5.0	-	-	4.2	10.6
2 adher.	120	1.2	4.0-5.0	80	-	4.2	10.6
3 Match	600	1.5	4.0-5.0	80	-	8.0/600	0/600
4 Hard	1200	2.0	4.0-5.0	106/300	3.2/300	8.0	-
5 Hard	1200	2.4	4.0-5.0	133/300	6.4/300	8.0	-
6 Hard	1200	2.7	4.0-5.0	160/300	12.2/300	8.0	-

In Fig. 4, there are shown, with respect to qualitative coating thickness, the profiles of the index of

refraction of optical devices according to Example 1 (prior art) and Example 2 (invention) and of the relative hardnesses for these Examples. For reasons of clarity, the adhesion- and index-matching coating layers are shown much too thick compared with the hard and wear protective coating areas and compared with the coating thickness in practice.

As shown in Fig. 2 and Table III, in Example 1 there is no index-matching coating layer. The index of refraction of Example 1, shown in dashed lines in Fig. 4, is 1.5 departing from the substrate and through the wear protective coating.

By means of the index-matching coating layer of Example 2, the index of the HI-substrate of 1.6 is continuously matched to the index of refraction of the wear protective coating, which is 1.5.

The measured transmission was again 92%, which shows that in spite of the difference of index of refraction between substrate and wear protective coating, there occurs no reflection at the substrate/coating interface which would lead to a measured overall transmission smaller than 92%. This value accords with the coating/air interface reflection of the wear protective coating with $n_D = 1.5$. Further, eye-inspection of the coated substrate showed no Newton ring pattern.

Again, the coated substrates were subjected to the mechanical tests mentioned above:

No rubber-gum traces appeared on the coating in contrast to considerable harm which was done by the rubber-gum test to the HI-plastic material substrate surface.

Example 3:

Bodies for optical lenses made of HI-plastic material with an index of refraction $n_D = 1.67$ were coated in the same way as has been described in connection with Example 2, with the exception that instead of M_2 there was applied the monomer M_3 during index-matching.

Again, the wear protective coated lenses were highly transparent, i.e. had a transmission of 92% and an end index of refraction of the wear protective coating of $n_D = 1.5$. With respect to Newton ring pattern and mechanical tests, the same results were achieved as have been described in connection with Example 2.

Fundamentally, it is essential that for index-matching between a substrate material of higher index of refraction and a coating with a lower index of refraction, the index-matching in the index-matching coating module is achieved by simultaneously reducing the proportion of that monomer gas which would lead to deposition of a coating material with a higher index of refraction when separately subjected to the defined plasmopolymerisation and increasing the proportion of that monomer gas which would lead to deposition of a coating material with a lower index of refraction when separately subjected to said plasmopolymerisation.

Example 4

The coated substrate according to Example 2 or 3 was additionally coated during further coating modules.

Thereby, the ratio of oxygen to dimethyldiethoxysilane (M_1) was further increased, and finally the coating process was performed with an

oxygen/dimethyldiethoxysilane ratio of at least 5, up to infinite. Thereby, on the wear protective coating according to Example 2 or 3, an adherence-improving coating was deposited and then an anti-reflection coating was applied in the form of a four-layer $\text{SiO}_2, \text{TiO}_2$ -broad-band anti-reflection layer system. The anti-reflection coating showed no peel-off tendency, tested with the well-known "Cross hatch tape test", as well as in the salt-water boiling test.

By the inventive method, a further advantage is achieved in that different material substrates may be coated by different coating processes so that finally the coating surfaces for all coated substrates have the same characteristics. Such characteristics may be mechanical, chemical and/or optical. Thus, by the mere fact that different material substrates, after having been coated, will have the same surface characteristics, it becomes possible afterwards to treat all these coated substrates equally.

The described method is especially suited for coating optical plastic material lenses. Thereby, lens bodies or substrates of different index of refraction may be coated with a wear protective coating so that the index of refraction continuously varies from the respective indices of the substrate materials to a common final index at the coating surface. Thus, in a subsequent coating process, as especially a subsequent anti-reflection coating process, lenses with optically different substrate materials may be commonly treated. Thereby a considerably improved exploitation of production capacity may be reached which may lead to lowering plant capacity, which is important for instance in small batch coating operations.

In contrast to the plasmapolymerisation coating methods known to date, by the inventive application of different monomer gases and of different other gases and by variation of the process atmosphere formed by such gases as a function of time, different characteristics, be they mechanical, chemical or optical, may simultaneously be varied along the coating thickness dimension. Especially by the use of titanium monomers it becomes possible to apply wear resistant, highly transparent (low absorption) coatings index-matched to high index of refraction ophthalmic plastic materials.

CLAIMS

1. An optical device, comprising a carrier substrate with a surface consisting of a material with a predetermined index of refraction and with first mechanical and/or chemical characteristics, said surface of said carrier substrate being coated, the surface of said coating remote from said surface of said substrate having second mechanical and/or chemical characteristics different from said first characteristics; wherein the index of refraction varies continuously through at least a part of said coating from said predetermined index of refraction of said substrate surface material to the final index of refraction at said surface of said coating.
2. A device according to claim 1, wherein said substrate consists of a plastic material.
3. A device according to claim 1 or claim 2, wherein said predetermined index of refraction of the substrate surface material is greater than 1.5.
4. A device according to claim 3, wherein the index of refraction of said substrate surface material is greater than 1.6.
5. A device according to any preceding claim, wherein said coating comprises a wear-resistant, hard material coating.
6. A device according to any preceding claim, wherein the transmission of said optical device in surrounding air is no more than 0.5% different from the transmission defined by said surface of said coating having said final index of refraction in surrounding air, for light with a

wavelength of 550 nm.

7. A device according to claim 5, wherein an anti-reflection coating is applied on said wear-resistant coating.

8. A device according to claim 7, wherein an adhesion improving intermediate coating is provided between said wear-resistant coating and said anti-reflection coating.

9. A device according to any preceding claim, wherein said substrate is the body of an optical lens.

10. A device according to any preceding claim, wherein said coating comprises, at least in an area in which said index of refraction varies from said predetermined value to said final value, at least one titanium-oxide compound.

11. A device according to any preceding claim, wherein said substrate is equally coated all around with the exception of at least one area at which said substrate was held during a process for depositing said coating.

12. A method for coating an optical substrate by plasmapolymerisation, comprising the steps of controlling the index of refraction along the growing coating so as to vary continuously from the index of refraction of said substrate to an intended final index of refraction of said coating, by varying the composition of the atmosphere of plasmapolymerisation and/or by varying at least one process parameter for said plasmapolymerisation process.

13. A method according to claim 12, comprising the step of simultaneously increasing the proportion of at

least one first monomer gas in said atmosphere and decreasing the proportion of at least one second monomer gas in said atmosphere, wherein said first and second monomer gases if separately employed in said plasmapolymerisation would lead to coatings of different indices of refraction.

14. A method according to claim 13, wherein the index of refraction of said growing coating is reduced from the index of refraction of said substrate material by selecting said at least one first monomer gas that would lead to a coating material of lower index of refraction if separately employed in said plasmapolymerisation.

15. A method of according to claim 13, wherein said at least one second monomer gas comprises at least one titanium compound.

16. A method according to claim 15, wherein said titanium compound is titanium(IV)-isopropylate.

17. A method according to any of claims 12 to 16, wherein the index of refraction of said substrate is greater than or equal to 1.6 and said final index of refraction of said coating is lower.

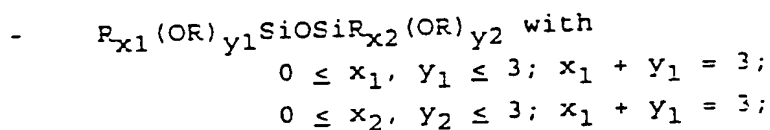
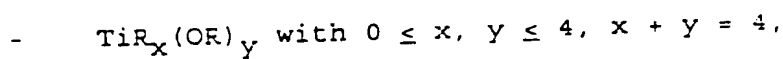
18. A method according to any of claims 12 to 17, further comprising the steps of applying a further coating to said coating, wherein the final index of refraction of said coating is equal to the index of refraction value of said further coating.

19. A method according to any of claims 12 to 18, wherein said process atmosphere comprises at least during a predetermined time-span one or more than one monomer in gas form and/or at least one further gas.

20. A method according to claim 19, wherein the further gas is oxygen or nitrogen.

21. A method according to any of claims 12 to 20, wherein one or more of the following monomers are applied to said process atmosphere: alkanes, alkenes, alkynes, alcohols, amines, ketones, cyclical or acyclical compounds as well as aromatic circular compounds, metalorganic compounds.

22. A method according to claim 21 wherein the metalorganic compounds comprise silicon or titanium compounds with the following structures:



wherein R stands for an organic group or a hydrogen atom and wherein at one metal atom different R-groups may be attached.

23. A method according to claim 21, wherein at least during varying said process atmosphere, the atmosphere comprises at least one of dimethyldiethoxysilane, toluene and titanium(IV)-isopropylate.

24. A method according to any of claims 12 to 23, wherein more than one substrate of different indices of refraction are coated and the index of refraction throughout the coating of each substrate is varied continuously to the same final index of refraction, whereby all said coated substrates may be equally treated subsequently.

Patents Act 1977
Examiner's report to the Comptroller under Section 17
(The Search report)

24

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Relevant Technical Fields

- (i) UK CI (Ed.N) C7F (FHB, FHE, FHX); G2J (JGBA1, JB7CX, JFI); C3T (TPH); C3R (R7N1)
- (ii) Int CI (Ed.6) C23C (16/00, 16/22, 16/50, 16/52) B05D (3/14, 7/24); G02B

Search Examiner
P G BEDDOE

Date of completion of Search
31 OCTOBER 1995

Databases (see below)

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

Documents considered relevant following a search in respect of Claims :-
1-24

(ii) ONLINE: WPI, EDOC

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- A: Document indicating technological background and/or state of the art. &: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages		Relevant to claim(s)
X,Y	GB 2015983 A	(GORDON) see especially Figure 3; Example 3	X = 1 Y = 12
X,Y	GB 1381644	(THOMSON) see especially Claim 1	X = 1 Y = 12
X,Y	EP 0521602 A1	(FORD) see especially Claim 1; and Examples	X = 1 Y = 12
X,Y	WO 85/01115 A1	(HUGHES) see especially Claim 1 and Examples	X = 1 Y = 12
X,Y	WO 83/01750 A1	(GORDON) see especially Example 1	X = 1 Y = 12
X	US 5217749	(WISCONSIN) see especially Claim 1; Examples; Figure 1	1, 12
X,Y	US 5154978	(TDK) see especially Examples	X = 1 Y = 12

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Continuation page

Category	Identity of document and relevant passages		Relevant to claim(s)
X,Y	US 4934788	(ROCKWELL) see especially Claim 1 and columns 2-6	X = 1 Y = 12
X,Y	US 4830873	(BOSCH) see especially Claim 1 and Examples	X = 1 Y = 12

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